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THE CLASSIFICATION OF CARBON COMPOUNDS

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CONTRIBUTIONS FROM THE COURSE IN PHARMACY

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PREFATORY REMARKS

“Arbeit allein kann die Licht gebenden Ideen nicht herbeizwingen. Etwas vom Schauen des Dichters muss auch der Forscher in sich tragen.”

Helmholtz.

“La science ne consiste pas en faits, mais dans les conséquences que l'on en tire.”

At the annual meeting of the Wisconsin Academy of Sciences, Arts, and Letters in December, 1894, the writer read a paper “On the Classification of Carbon Compounds,” which was published in the Transactions¹ of that body. The introductory paragraph may here be quoted:

“In the winter semester of 1888–9, Professor August Kekulé, in his course on the chemistry of the carbon compounds at the University of Bonn, Germany, introduced the subject of fatty alcohols, aldehydes, ketones, acids, hydroxy acids, etc., by a lecture in which he gave a general survey of the theoretically possible hydroxy derivatives of the paraffin hydrocarbons. I suppose it was Prof. Kekulé’s usual method of treating the subject, but I am not warranted in making so broad a statement. However, this theoretical introduction is fully in harmony with the methods of teaching of this genial lecturer, known and celebrated not so much for the compounds he has discovered, but for

¹ Vol. 10, p. 310. A second paper was read ten years later, but not published. At the Baltimore meeting of the American Chemical Society in 1909, a twenty-minute paper on the same subject was read by request at a general meeting of the Association.

his theories, that have prophesied the possibility of hosts of compounds, which have been prepared by others in the attempt to establish as well as in the attempt to overthrow Prof. Kekulé's theories."

If honest confession be good for the soul, the above paragraph ought to suffice to show that the writer makes no great claim for originality and at the same time it reveals the source of his inspiration. All that the writer claims is that he has endeavored to systematize by means of logical questions and answers.

The problem of rational classification of the carbon compounds is one of those that can not be worked out in the research laboratory, but has to be solved primarily in the class room. Now, that after more than twenty years of experience in this direction the system has revealed its advantages not only in the class room of the writer but in the class rooms of his former students as well, the time seems to have arrived when the more completely worked out system should be given wider publicity.

However, while the system had to be tried out in the classroom, the conference, and the seminar, it has found useful application in laboratory research. As applied to the sesquiterpenes,² as representatives of the hydrocarbons, it has evidently proven acceptable to others.³

In the systematic study of the glucosides, pigments, and alkaloids it has brought out relationships formerly not apparent. An attempt is also being made to make the organic laboratory manual something more than a collection of working formulas, and suggestions for reading. As to details, the writer hopes to find the time to bring the entire *materia phytochemica* into conformity with this system and thus to show the numerous practical as well as theoretical advantages which it possesses.

It may be suggested that the time is not opportune for a revision of the classification of carbon compounds on the basis of structural atomic chemistry, since the atoms are about to be replaced, in chemical thought, by electrons. Such a suggestion, however, is not likely to be well received so long as even

² O. Schreiner, *The sesquiterpenes*, p. 17.

³ Comp. "*Neuere Eintheilung der Sesquiterpene*" in Arnold Lewinsohn, *Beitraege zur Kenntniss der Sesquiterpene*, Innaugural-Dissertation, Leipzig, 1908, p. 14.

physicists warn chemists "not to be too ready to throw away conceptions (such *e. g.*, as that of an atom) . . . that have proved very valuable as aids to the advancement of science in the past."⁴

However valuable the theory of electrons may prove, it may be a generation or more before it can affect our ideas of the classification of carbon compounds, should it ever exert such an influence. While we should always welcome new tools and learn to use them if possible, it would be foolish indeed to discard an old tool, simply because a new one, which we have not learned to use, is in sight.⁵

All that the writer asks for the suggestions toward the rational classification of the carbon compounds is that they be given a fair trial. He fully realizes that in such matters changes are not likely to come about with revolutionary suddenness, but that old habits of thought must be gradually overcome by the slow process of evolution.

DEFINITION OF ORGANIC CHEMISTRY

For the purpose of this study organic chemistry is defined as the chemistry of the hydrocarbons and their substitution products. Not that this definition covers ground other than that covered by the definition mostly in vogue at the present time, *viz.*, that organic chemistry is the chemistry of the carbon compounds, but that the definition suggested has this advantage in the study of classification and nomenclature that it emphasizes two important lines of thought and development. First, it emphasizes the fact that the hydrocarbons, the simplest of carbon compounds, are to be regarded as basal compounds and that all other carbon compounds are to be derived from these hydrocarbons by the process of substitution.

⁴ President Richard G. MacLaurin of Mass. Inst. of Tech. at the banquet of the A. C. S. Science, 32, p. 10.

⁵ It would be more than foolish for the accomplished piano player to abandon his instrument at the age of twenty-five or more because he has become convinced that the violin is the more perfect musical instrument. While a successful pianist, he might, and, in all probability, would, achieve only mediocrity with the violin. The same reasoning applies to the present day chemist and his *possible change from the atomic to the electron theory.*

Kolbe at one time suggested that all carbon compounds be derived from carbon dioxide from which the plant synthesizes its complex carbon compounds. But though we could follow the synthetic processes of the plant much better than we can even today, no one would any longer think of following such a suggestion for purposes of classification or nomenclature. Our knowledge of the hydrocarbons, however, is such that today they universally serve as the basal compounds, not only for purposes of classification and nomenclature but for didactic purposes as well. What we need at present is a more rational classification of these basal hydrides of carbon than is commonly found in organic chemical literature.

The second basal thought suggested by the definition is, as already pointed out, that all other carbon compounds be derived from the hydrocarbons by the process of substitution. In research work, in preparation work, and also in analytical processes we make extensive use of the additive capacity of compounds.

We need in no wise underestimate the importance of the addition product because addition is not universally applicable, yet this is more than sufficient reason for not adopting it as a basal process in a system of classification and nomenclature. Neither can we for this purpose adopt advantageously any other than a unitarian point of view. What we need in organic classification and nomenclature is to get rid, for the purpose under consideration, of points of view based on totally different conceptions, such as the old dualistic view of acids, bases, and salts, that of the theory of types, etc.

The term organic chemistry is said to have been introduced by Bergmann who pointed out that there was no fundamental difference between the chemical compounds from the vegetable and animal kingdoms. Previous to his time the *materia chemica*, and with it chemical science, was divided according to the source of the material from the mineral, vegetable, and animal kingdoms. In this chemists had followed the suggestion by Emanuel, who in 1682 classified all terrestrial objects according to their relation to one of these natural kingdoms. However, organic chemistry was long thereafter still subclassified into vegetable chemistry and animal chemistry.

The student of organic chemistry is usually told that by his so-called synthesis of urea, Woehler in 1828, dealt the death-blow to the notion that organic chemistry is the chemistry of the functions of organs and their products, in other words of that mysterious something called life. Yet Woehler's so-called synthesis was no synthesis at all, but an inversion, an intramolecular re-arrangement of the atoms of one molecule to another of like size. Neither did Woehler's noteworthy and far-reaching observations immediately influence chemical thought, at least so far as definition and classification reflected the advance of chemical thought. Even Gmelin stated that "the bodies of the organic kingdom are distinguished in their most complete state, from those of the inorganic kingdom . . . by being composed, for the principal and most important part at least, of chemical compounds quite peculiar to them, called organic compounds . . ."¹

Today we have gotten away completely from any significance of life so far as the concept organic chemistry is concerned. That branch of chemistry which deals with the so-called life processes of plants and animals is termed biochemistry and represents a line of chemical activity as does phytochemistry and zoochemistry. Organic chemistry is universally interpreted at present as implying the chemistry of the carbon compounds irrespective of source or mode of formation. The term carbon has reference to elemental composition and could not have been used before the recognition of the modern elements since the close of the 18th century. Indeed, its use in the sense as quoted above is of much more recent date. The first to have suggested the definition of organic chemistry as the chemistry of carbon appears to have been Gerhardt as early as 1844 or possibly earlier.² Kekulé then suggested that we "define organic chemistry as the chemistry of the carbon compounds."³ This definition-subtitle was accepted by Richter, one of the disciples of Kekulé and author of the well-known text which has been re-

¹ For a more detailed statement see Appendix: *Definitions of organic chemistry.*

² See Appendix: *Definitions of organic chemistry.*

³ See Appendix: *Definitions of organic chemistry.*

peatedly revised by Anschuetz and translated into English by Smith.⁴

As a mere definition this will do as well as any other especially if interpreted in the light of Kekulé's commentary,⁵ but if our definition is to point logically to the method of classification, as the classification should reflect the most satisfactory chemical theories, then it is no longer satisfactory for purposes such as are here to receive consideration. Hence for our present needs we prefer to define organic chemistry as the chemistry of the hydrocarbons and their substitution products. A careful perusal of the principles of classification will, no doubt, be found to justify the adoption of this definition which is equally valuable from a didactic point of view.

HISTORY OF ORGANIC CHEMICAL CLASSIFICATION

In order to give proper expression to chemical ideas, a chemical language has been developed which reflects chemical thought. Science, we are told, consists not of facts, but in the conclusions which we draw from them. Some of the most important conclusions drawn from chemical facts have been derived by systematization of the *materia chemica*. As a result, general theory and chemical classification have developed side by side, so that the study of the history of classification reflects in no small part the advance made in general chemical theory.

A review of the principal systems of classification of the past hundred years and more, clearly reveals the fact that the rational systems of classification were based largely on structural theories, structural of necessity, in the varying sense in which this concept was interpreted from time to time. The temporary breakdown of structural conceptions during the middle of the nineteenth century, when atoms had to give way to equivalents, gave rise to a condition bordering on anarchy not only in classi-

⁴ Victor von Richter's *Organic Chemistry or Chemistry of the Carbon Compounds*. Edited by R. Anschuetz. Authorized translation by E. F. Smith, 1899.

⁵ See Appendix: *Definitions of organic chemistry*.

fication but in general chemical thought. The arrangement of carbon compounds according to the number of carbon atoms* is no more a rational classification than the arrangement of plants according to the number of the stamens of their flowers. Such an artificial arrangement, while of value in the tracing of analytical results based on elementary analysis¹ does not afford for most purposes even the convenience of the alphabetical arrangement of the chemical dictionary or encyclopedia.

Previous to the chemistry of oxygen, as elucidated by Lavoisier, there was no organic chemistry in name, and but few carbon compounds had been isolated or prepared artificially.² Yet in order to understand later developments, it seems advisable to go back as far as Lemery and one of the first chemical texts free from alchemistic jargon, his *Cours de chimie*.

Following the classification of all natural objects (and beings) into three natural kingdoms, the *regna naturae*, suggested by Emanuel in 1682, Lemery arranged the subject matter of his Course in Chemistry under these headings:

- (1) Upon minerals
- (2) Upon vegetables, and
- (3) Upon animals.

As early as 1780, Bergmann began to distinguish organic from inorganic bodies, having shown that the same organic substances can be obtained from both the vegetable and animal kingdoms. Nevertheless, the classification of the organic *materia chemica* according to the two kingdoms of organized nature, namely the vegetable and animal was upheld for a long time.

Thus Lavoisier, whose principal point of view was that of oxygen first, last, and all the time, separates the carbon-containing acids obtained from the vegetable kingdom from those obtained from the animal kingdom. This separation is found even in the third, rewritten and revised edition of Lavoisier's "*Traité élémentaire de chimie*" of 1801.

Fourcroy, one of Lavoisier's associates on the Commission of Chemical Nomenclature according to the antiphlogistic system,

* See Appendix: Arrangement according to number of carbon atoms.

¹ Compare Richter's *Lexikon der Kohlenstoff-Verbindungen*, and the Formel-register of the *Berichte der deutschen chemischen Gesellschaft* based on the same principle.

² See Appendix: Classification as revealed by tables of contents.

likewise distinguished between "*les composés végétaux*"³ and the "*substances animales*."⁴

Berzelius, the great generalizer of his time, in his epoch-making "*Lehrbuch der Chemie*" does likewise, even in the third edition published in 1837. His organic chemistry is subdivided into "*Plant Chemistry*"⁵ and "*Animal Chemistry*."⁶

With such classical examples as guides, it is not surprising that other authors followed even up to the middle of the nineteenth century. Thus this system of classification long outlived its theoretical usefulness.

Whatever may be said for or against the designation of Lavoisier as the founder of chemical science, this much is undeniably true that his antiphlogistic theories placed chemical classification and nomenclature on a new basis. As already pointed out, the chemistry of Lavoisier was the chemistry of oxygen just as the predominant chemistry of Kekulé and of the generation of chemists that followed him was a chemistry of carbon, even more so. The oxides of the metals were designated bases, the oxides of the nonmetals, acids, both binary compounds, and the union of the two resulted in the ternary compounds or salts which naturally also contained oxygen. Thus there was laid the foundation for the electrochemical theories of Davy and the dualistic structural theories of Berzelius. The discovery of the halogens and their derivatives naturally modified these views but they did not revolutionize them. Indeed we today are still under the ban of the antiquated theory of acid, base and salt.

Compared with the inorganic field, organic chemistry as defined by Bergmann played but a minor role though it was being enriched by Scheele and other phytochemists. Yet organic chemistry had its organic acids comparable to the inorganic acids, it also had its inorganic salts of these organic acids. The organic base, however, was wanting until Sertuerner discovered it in morphine, this "new salifyable plant base" as he called it. This morphine attracted universal attention, not because it had been

³ Systeme des connaissances chimique (Bumaire, An. IX), tomes 7 et 8.

⁴ Ibidem, tomes 9 et 10.

⁵ Vols. 6, 7 and 8 of the 3rd German edition of 1837.

⁶ Vol. No. 9 of the same edition.

isolated from opium, for such isolation had been effected independently by both Derosne and Sertuerner more than a dozen years before, but because Sertuerner had recognized its basic, *i. e.*, its salt-forming properties. Thus the parallel between organic chemistry and inorganic chemistry was thought to have been established.

This satisfaction, however, was of but short duration for chemists soon realized the importance of the fact, already hinted at by Sertuerner, that morphine and the alkaloids discovered in rapid succession, were related to the inorganic ammonia, rather than to the oxygen bases of the metals.

The conception of this parallel, however, seemed too good to be abandoned, so it was revived by Liebig who pointed out that the organic alcohol was the true analogue of the inorganic base as the organic acid was that of the inorganic oxygen acid. In like manner the product of the union of organic acid and alcohol, the ethereal salt or ester, was regarded as the analogue of the inorganic salt. Thus there was re-established the true analogy between organic chemistry and inorganic chemistry, and organic chemistry was defined the chemistry of the compound radicle by Liebig, the alkyl or positive radicle corresponding to the metal, the acyl or negative radical to the non-metal.

Whereas the difficulties of the inorganic system were patched up by coining new names, such as halogen acids and halides, thioacids and thionates, the difficulties of the organic field would not be downed by coining such words as neutral principles, *i. e.*, substances that were neutral in themselves and not by virtue of the neutralizing power of acid upon alkali or *vice versa*. Yet in organic chemistry as in inorganic chemistry we are still laboring under the ban of opposites, of acids and alcohols, which instead of being regarded primarily as opposites should rather be looked upon as related compounds.

The difficulties arising from the ever growing number of carbon compounds were not solved by creating new classes of compounds or by relegating them to an ever convenient lumber chamber. The conception of the rigid radicle, this element, so-called, of organic chemistry, had to be abandoned in the light of the theory of substitution. The concept of homology, though

it aided materially in throwing light on difficult problems, did not remove the more fundamental difficulties of the situation. Neither did the theory of types, though it, more than any one other conception, aided in bringing order into chaos, and though it paved the way for the structural theories of Kekulé.

All of these theories and views are reflected in chemical nomenclature and classification. These reflections are found not only in the chemical history of the past century, but in our present day mode of chemical thought and language. While useful at times, they often linger as an obstructing "*spuk*," just as the life "*spuk*" of organic chemistry has made its presence felt again and again and has not been downed completely even today. The manner in which these ideas are reflected in chemical classification can best be seen from the tables of contents of contemporary treatises on chemistry.

The structural conceptions of Kekulé are too well known to be reviewed here. How he arrived at them he himself has told us in his after dinner speech of 1890 at the celebration of the twenty-fifth anniversary of the benzene theory.⁷ How he worked out his structural or graphic formulas is best shown in some of the considerations of the next chapter.

Frankland having recognized the tetravalence of the carbon atom, Kekulé added the type methane to the older types ammonia, water, hydrohalogen and hydrogen. The structural conception of the hydrocarbons of the methane series and of their halogen and hydroxy substitution products resulted. These, together with the olefine and acetylene hydrocarbons and their respective derivatives were grouped together as fatty compounds. His conception of the structure of benzene added still a new type and its homologues and their derivatives were grouped together as aromatic compounds.

Great as was the advance made by Kekulé in his classification there is today no more justification in adhering to it than to the notion of acids and bases. Both conceptions emphasize opposites whereas the relation of gradual evolution is the important point to be emphasized. Opposition becomes apparent

⁷ *Berichte*, **23**, p. 1306. For an English translation see the Kekulé lecture by Jepp in the *J. C. S.* **73**, p. 100 of Transactions.

only when we take two compounds or classes of compounds out of their natural surroundings and contrast them by ignoring the intervening links. In an age of evolution such a method of procedure is as fundamentally wrong in chemistry as it is in biology.

A PROPOSED BASIS FOR THE RATIONAL CLASSIFICATION OF CARBON COMPOUNDS

CLASSIFICATION OF THE HYDROCARBONS

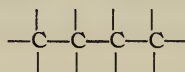
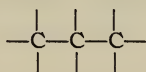
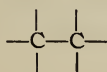
Assuming the tetra-valence of the carbon atom, there is but one hydrocarbon in which all four of the affinities of the carbon atom can be saturated by hydrogen. The four affinities may be indicated in the plane of the printed page by four lines in the

following manner: $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$. If these affinities are saturated by

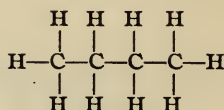
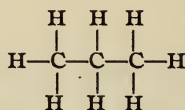
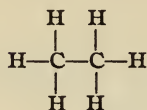
hydrogen we get the formula for methane or marsh gas, CH_4 or

$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$. In place of saturating these four affinities with hy-

drogen, or *e. g.*, with halogen or oxygen, it may be assumed that one or more may be satisfied by the same number of valencies of other carbon atoms. Assuming for the present that the carbon atom be united with other carbon atoms by single affinities only, we get the following carbon nuclei with their free affinities:

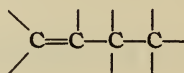
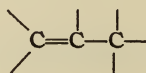
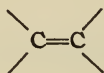


If these free affinities are now satisfied by hydrogen, the following hydrocarbons result:

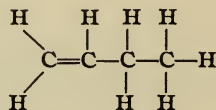
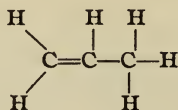
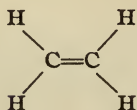


It will be seen at once, that each carbon atom is united with two hydrogen atoms, and that the two end carbon atoms have a third affinity satisfied by hydrogen. For n carbon atoms there are, therefore, $2n + 2$ hydrogen atoms in each molecule. Hence, the general formula for these and like hydrocarbons will be $\text{C}_n\text{H}_{2n+2}$. Having assumed a tetra-valence for the carbon atom this will, therefore, be the limit series of hydrocarbons (*Grenzkohlenwasserstoffe*). We can imagine but one such series and only one is known.

If in place of uniting two carbon atoms of the same molecule by a single bond, we imagine them united by two bonds the following carbon nuclei will result:



If the free affinities be now satisfied by hydrogen atoms the following hydrocarbons are obtained:

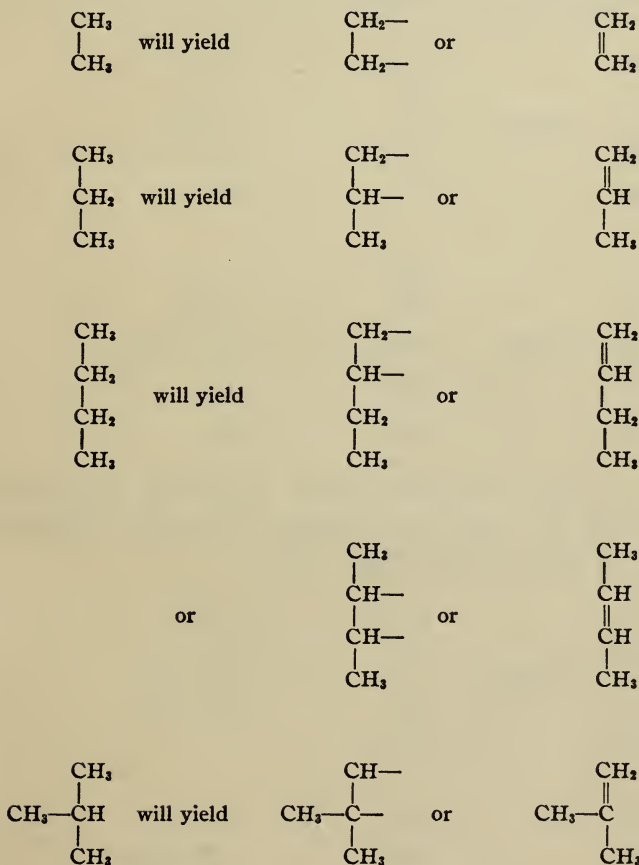


The addition of the carbon and hydrogen atoms in each molecule will show that these hydrocarbons contain two hydrogen atoms less than the hydrocarbons with the same number of carbon atoms first developed. Their general formula will, therefore, be:

$$\text{C}_n\text{H}_{2n+2} - \text{H}_2 = \text{C}_n\text{H}_{2n}.$$

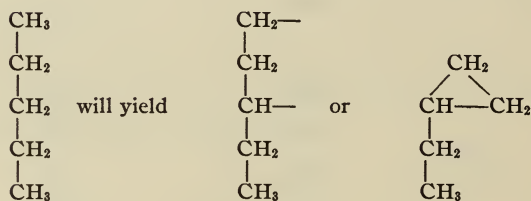
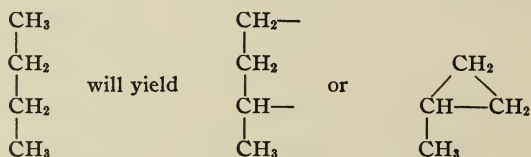
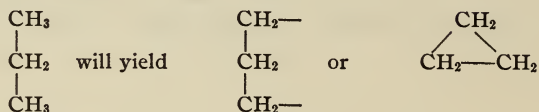
Hence we can derive the hydrocarbons of the formula C_nH_{2n} from the hydrocarbons of the formula C_nH_{2n+2} by the abstraction of two hydrogen atoms.

This abstraction of hydrogen atoms may take place first of all in connection with neighboring carbon atoms. Thus

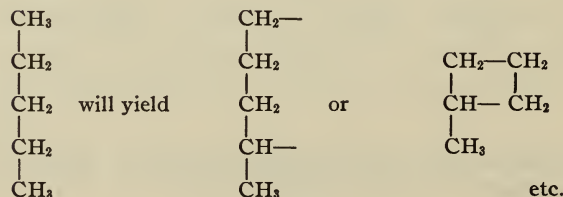
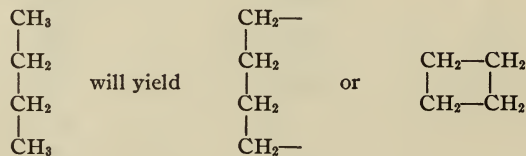


These hydrocarbons are identical with those derived by the previous method.

Secondly, the two hydrogen atoms may be abstracted from carbon atoms that are not neighboring but have one other carbon atom intervening. In that case

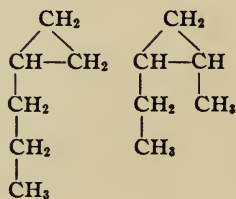
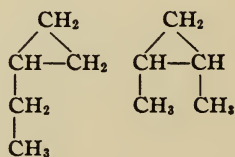
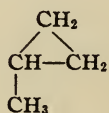
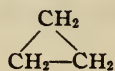
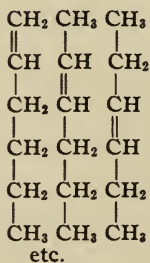
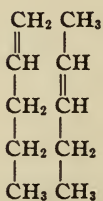
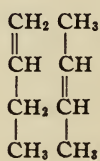
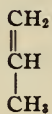
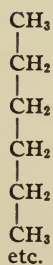
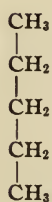
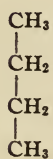
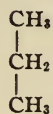
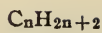


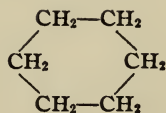
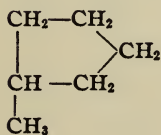
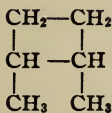
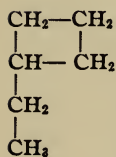
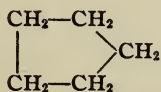
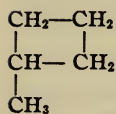
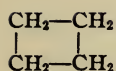
If next we allow two carbon atoms to intervene between the carbon atoms from which the hydrogen atoms are abstracted the following cyclic hydrocarbons result:



Next we may allow three, four or more carbon atoms to intervene and cyclic hydrocarbons with five, six and more members to the cycle will result.

Proceeding from normal hydrocarbons of the methane series the following hydrocarbons are obtainable. The cyclic members are classified according to the number of carbon atoms to the cycle and are tabulated so as to show the isomerism of the hydrocarbons with the same number of carbon atoms.





A second dimethyl cyclobutane has been omitted for want of space.

Whereas of the formula of saturation $C_{2n}H_{2n+2}$ but one series of hydrocarbons is possible, and representatives of but one series are known; of the formula of saturation C_nH_{2n} , one chain series and an indefinite number of cyclic series can be developed. Representatives of the chain series and of four of the cyclic series are known. Derivatives of still another series with seven carbon atoms to the cycle are likewise known.

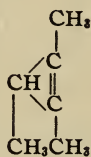
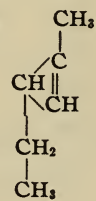
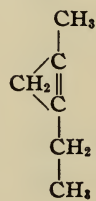
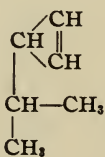
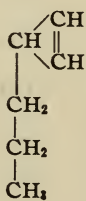
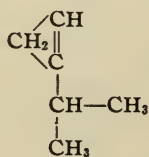
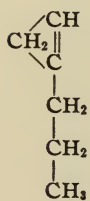
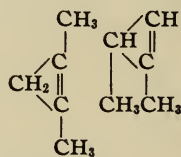
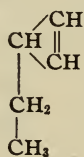
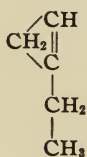
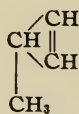
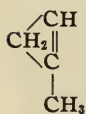
The names of the normal chain hydrocarbons and initial members of the cyclic series are commonly given in accordance with the principles of the Geneva Congress.

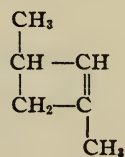
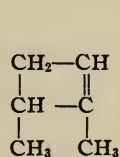
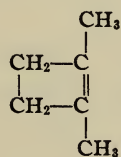
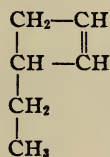
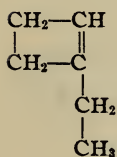
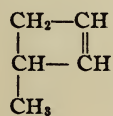
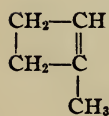
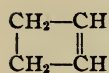
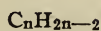
If we now proceed one step farther and abstract two more hydrogen atoms we arrive at the formula of saturation C_nH_{2n-2} . Under this formula two unsaturated chain series and the following unsaturated monocyclic series and saturated dicyclic series may be developed.

In the following tabulations some of the isomeric forms have been omitted for want of space on the page on which they belonged. All isomeric forms with the double bonds in the side chains have been omitted for the same reason. These tables have been compiled, not with any idea of completeness, but rather for the purpose of affording a convenient oversight such as seems necessary for a proper grasp of the situation.

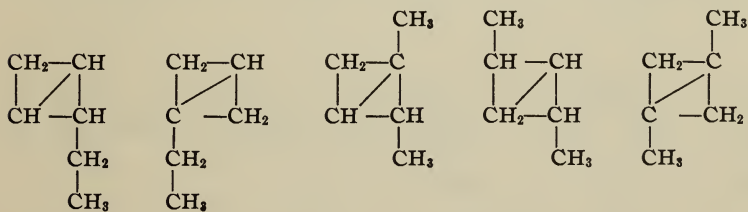
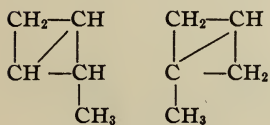
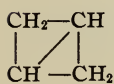
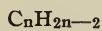
C _n H _{2n-2}			
F		F F	
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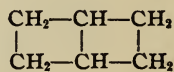
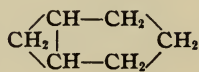
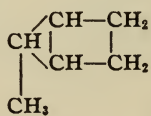
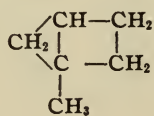
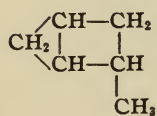
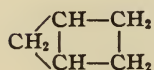
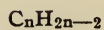


$$F\Delta$$




C_nH_{2n-2}	
$F\Delta$	
$ \begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CH}_2-\text{CH} \\ \diagdown \text{CH}_2-\text{CH} \end{array} \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{CH}_2 \end{array} $	
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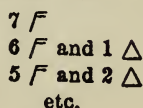
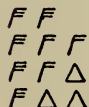
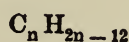
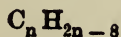
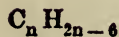
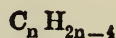
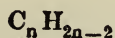
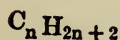




It is not necessary to carry the details of this process any farther, if we but realize the important conclusion that can be derived from the few instances cited, *viz.*, that the structural equivalent of two hydrogen atoms is either a double bond or a cycle, also that in place of two double bonds we may have still another structural equivalent, the treble bond.

Bearing this in mind, we can readily classify under each formula of saturation the groups of series of hydrocarbons. In the following table these groups are indicated with the use of the following symbols:

F = double bond
 Δ = cycle
 F = treble bond.



Hence, the hydrocarbons may be rationally classified

Firstly, According to their degree of saturation;

Secondly, According to their chain or cyclic character;

Thirdly, According to the number of carbon atoms.

CLASSIFICATION OF THE SUBSTITUTION PRODUCTS
OF THE HYDROCARBONS

Having outlined very briefly, the principles that should govern us in a rational classification of the basal carbon compounds, the hydrocarbons, we are now prepared to classify their substitution products.

In the large number of known hydrocarbons and in the thousands of unknown but possible hydrocarbons we have, in addition to carbon atoms that have their four affinities saturated exclusively with the affinities of other carbon atoms, the following three simple hydrocarbon groups:

- CH₃, the univalent methyl group
- =CH₂, the bivalent methylene group
- ≡CH, the trivalent methenyl or formyl group

As has already been pointed out, methane constitutes the single exception to this rule. Hence its substitution products or derivatives differ somewhat from the analogous derivatives of other hydrocarbons.

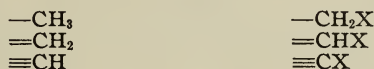
Inasmuch as we are going to regard all carbon compounds as substitution products, direct or indirect, of the underlying hydrocarbons, all direct substitution must take place in connection with one of these three simple groups. This suggests at once one of the basal ideas of classification.

Even more fundamental, however, is the conception of how often substitution has taken place. Inasmuch as it is the univalent hydrogen of the hydrocarbon that is replaced step by step, the unit of substitution must be a univalent atom or radicle. Accordingly we distinguish between mono-, di-, tri-, tetra-, etc., substitution products. This is done irrespective of the substituting element or radicle.

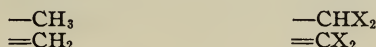
In order to illustrate the principles involved, substitutions with univalent elements also with the univalent hydride radicles of divalent and trivalent elements will be effected.

HALOGEN SUBSTITUTION PRODUCTS

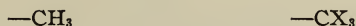
For substitution with a univalent element, the halogens are best adapted. Of mono-halogen substitution products there must be three types, since all three simple hydrocarbon groups contain at least the one hydrogen atom necessary for mono-substitution.



Whereas mono-substitution can take place only in connection with one carbon atom, di-substitution can take place in connection with either one or two carbon atoms. If it takes place in connection with the same carbon atom, two types of di-substitution products are possible, and only two, for but two of the three simple hydrocarbon groups contain the requisite two hydrogen atoms, *viz.*



Tri-halogen substitution can take place in connection with one, two or three carbon atoms. If it takes place in connection with the same carbon atom, but one type of tri-halide is possible, since but one of the three simple hydrocarbon groups contains the requisite number of hydrogen atoms to admit of tri-substitution, *viz.*



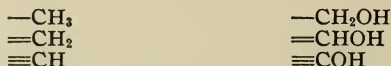
With the exception of methane, which, with its derivatives, as has already been pointed out, must occupy an exceptional position in any rational classification, tetra-substitution cannot take place in connection with one and the same carbon atom. Hence the possibilities of substitution in connection with one and the same carbon atom are exhausted with tri-substitution. Substitution in connection with different carbon atoms will be considered later. Suffice it for the present to state that no new types are created by substitution in connection with different carbon atoms. The isomerism thus produced is one of position.

The influence of position on the structure of a molecule is a study by itself and should not be confounded with that of simple types.

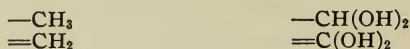
HYDROXY SUBSTITUTION PRODUCTS

Among the divalent elements of organic chemistry, oxygen is undoubtedly the most important. Inasmuch as the unit of substitution in the underlying hydrocarbon is the univalent hydrogen atom, it would not be rational to replace, step by step, hydrogen atoms by their oxygen equivalents. Substitution, however, can be rationally effected by a univalent oxygen-hydrogen radicle, such as we possess in the hydroxy or hydroxyl group, *viz.* the (—O—H).

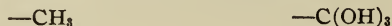
The simplest kind of hydroxy substitution product will naturally be the mono hydroxide. As of mono-halides, and for the same reason, there are three types of mono-hydroxides or alcohols. They are represented by the following type formulas:



Of di-substitution products, in which the di-substitution has taken place in connection with the same carbon atom, two types of dihydroxides, or glycols, are possible, *viz.*



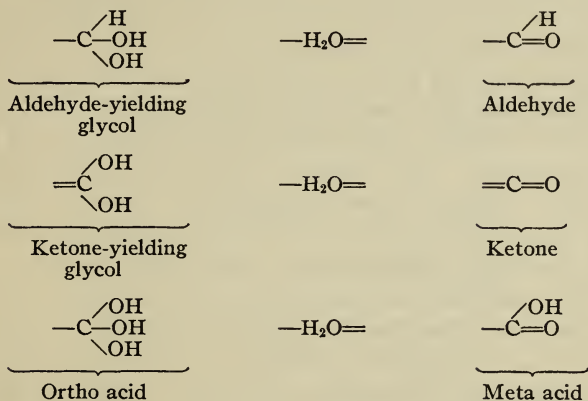
Of tri-hydroxides, in which all three hydroxy groups are connected with the same carbon atom, but one type is possible, *viz.*



Such a tri-atomic alcohol in which all three hydroxy groups are connected with the same carbon atom is known as an ortho acid.

It is a well known fact in organic chemistry that, whenever two or more hydroxy groups are connected with the same carbon atom, a tendency manifests itself to split off the elements of a molecule of water, a tendency readily interpreted with the aid of the thermochemical equation of water.

The two glycols, also the ortho acid, are subject to such dehydration as indicated by the following type formulas:



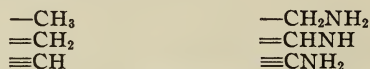
There are, therefore, as many as nine simple types of oxygen substitution products: six hydroxy substitution products, which, together with their dehydration products are herewith tabulated.

Hydrocarbon groups	Mono-hydroxides	Dihydroxides	Trihydroxides
—CH ₃	$\begin{array}{c} \text{H} \\ \diagup \\ \text{—C—H} \\ \diagdown \\ \text{OH} \end{array}$ Methyl.....Primary alcohol	$\begin{array}{c} \text{H} \\ \diagup \\ \text{—C—OH} \\ \diagdown \\ \text{OH} \end{array}$ Aldehyde.....Aldehyde-yielding glycol	$\begin{array}{c} \text{OH} \\ \diagup \\ \text{—C—OH} \\ \diagdown \\ \text{OH} \end{array}$ Ortho acid
			$\begin{array}{c} \text{H} \\ \diagup \\ \text{—C=O} \\ \diagdown \\ \text{OH} \end{array}$ Aldehyde.....Meta acid
=CH ₂	$\begin{array}{c} \text{H} \\ \diagup \\ \text{=C—OH} \end{array}$ Methylene Secondary alcohol	$\begin{array}{c} \text{OH} \\ \diagup \\ \text{=C} \\ \diagdown \\ \text{OH} \end{array}$ Ketone-yielding glycol	
			=C=O Ketone
≡CH	$\equiv\text{COH}$ Methenyl.....Tertiary alcohol		

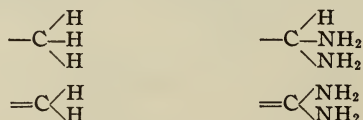
AMIDO SUBSTITUTION PRODUCTS

Of the trivalent elements, nitrogen is unquestionably the most important in organic chemistry. However, it is not practicable to substitute, even in a theoretical way, one-third and two-thirds of a nitrogen atom for one and two hydrogen atoms, respectively. The simplest univalent nitrogen-hydrogen radicle, the amido or amino group, however, may replace the hydrogen of an underlying hydrocarbon. As a matter of fact, it is with compounds such as these that the organic chemist has to deal. Hence the nitrogen derivatives can best be studied as amido substitution products and their deammoniated compounds.

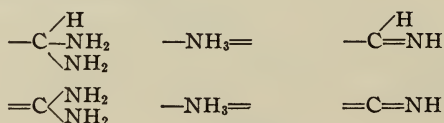
As with the halides and hydroxides, the monamides come first. Also, as with the mono-halides and mono-hydroxides, there are three types of monamides, according to the replacement of a methyl, methylene, or methenyl hydrogen atom, as indicated by means of the following formulas:



In connection with the diamines we must again distinguish between those diamides in which the two amido groups are connected with the same carbon atom, and those in which they are connected with two carbon atoms. The former only are here considered. Of these there are again two types as of the corresponding di-halides and di-hydroxides, *viz.*

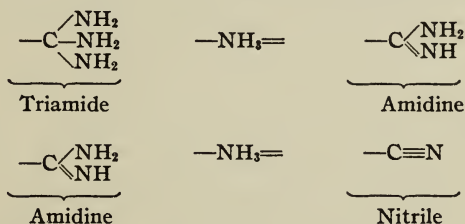


In like manner as the corresponding di-hydroxides readily split off the elements of a molecule of water, so the diamides, (though with less readiness) split off the elements of a molecule of ammonia, yielding the corresponding imides as indicated by the following formulas:



These two imides correspond to the aldoximes and ketoximes, respectively.

Of the triamides, in which the three amido groups are connected with the same carbon atom, but one is derivable, *viz.*, that from the methyl group, which is the only simple hydrocarbon group containing the requisite number of hydrogen atoms. By splitting off ammonia it may yield first the amidine, and then the nitrile, as indicated by the following formulas:



In the following table the simple types, ten in all, of the amido substitution products and their deammoniated compounds are given:

Hydrocarbon groups	Monamides	Diamides	Triamides
$\begin{array}{c} \text{H} \\ \diagup \\ \text{—C—} \\ \diagdown \\ \text{H} \end{array}$	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{—C—} \\ \diagdown \\ \text{H} \end{array}$	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{—C—} \\ \diagdown \\ \text{H} \end{array}$	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{—C—} \\ \diagdown \\ \text{NH}_2 \end{array}$
$\text{=C}\begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array}$	$\text{=C}\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{H} \end{array}$	$\text{=C}\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{NH}_2 \end{array}$	$\text{—C}\begin{array}{c} \text{NH} \\ \diagup \\ \text{H} \end{array}$
$\equiv\text{CH}$	$\equiv\text{CNH}_2$	=C=NH	$\text{—C}\begin{array}{c} \text{NH} \\ \diagup \\ \text{NH}_2 \end{array}$
			$\text{—C}\equiv\text{N}$

The possibility of splitting off ammonia in a different manner will not be discussed at this point.

OTHER SUBSTITUTION PRODUCTS

With the halogen substitution products, we have disposed, with the exception of manganese, of the known elements of the seventh group of the periodic system, *i. e.*, so far as the simple ele-

mental substitution products are concerned. These constitute by far the bulk of halogen organic compounds.

Like the oxygen derivatives, so the sulphur, selenium, and tellurium derivatives can be derived by the substitution of their simple hydride groups for hydrogen, and the subsequent splitting off of sulphuretted hydrogen, etc. Such compounds as sulphates, sulphites, etc., are easily derived as are the corresponding derivatives of the inorganic acids.

Analogous to the amides are the phosphines, arsines, etc. What has been said of the sulphates applies also to phosphates, arsenates, etc.

We now arrive at the fourth group of the periodic system. The typical organic element of this group is carbon. Its simplest univalent hydride group is the methyl group. By the substitution of this methyl group for a hydrocarbon hydrogen we obtain a homologue of the hydrocarbon in question. This brings us back to the hydrocarbons.

The classification of substitution products obtained by the substitution of elements of groups three, two, one, and eight, need not concern us at present.

GENETIC RELATIONSHIP OF TYPES

We have thus far reduced the large bulk of simple carbon compounds to relatively few types. While it should always be remembered that the properties of a compound are functions of its structure, and that the structure of a compound implies more than the peculiar characteristics of the type or types to which it belongs, yet the type is of fundamental importance. It is essentially the same irrespective of degree of saturation, of chain or cyclic character, and of the number of carbon atoms. Differences are primarily differences of degree. All of these factors, however, exert a modifying influence, as does also the piling up of a number of the same type groups within the same molecule.

These are matters to be brought out later, at least in so far as they exert an influence on the mode of classification. For the present, however, we are concerned with simple types only.

The advantages of the system of classification thus far outlined are those of simple logical questions and answers, based

on a definition that foreshadows the questions. Organic chemistry being defined as the chemistry of the hydrocarbons and their substitution products, the latter are naturally classified into mono-, di-, tri-, etc., substitution products, that is, according to the number of times substitution has taken place, irrespective of the substituting element or radicle. Taking into consideration that there are three simple hydrocarbon groups of which all hydrocarbons are made up, it follows that there must be three types of mono-substitution products. For the same reason there are two types of di-substitution products, and but one of tri-substitution products in which substitution has taken place in connection with the same carbon atom. If substitution takes place in connection with different carbon atoms, no new simple types, as has already been pointed out, are formed.

A system of classification based on rational questions and answers should certainly be a gain over a mode of classification based on several historical systems. While different points of view are not only an advantage, but a necessity, in the study of chemistry, in the classification of compounds a unitarian point of view should be maintained if possible.

But even such a gain might not be worth the trouble involved in a change if the system proposed did nothing more than to effect a systematic pigeonholing of chemical compounds. A rational classification based on chemical structure, and on the theory that the properties of a chemical compound are functions of its structure, must accomplish much more. It must bring out the genetic relationship of the different types.

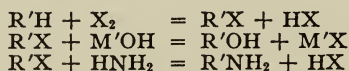
This genetic relationship can be brought out in several ways. Suffice it for the present to bring out the relationship between the simple underlying hydrocarbon groups and the types of the three classes of mono-, di-, and tri-valent elements utilized thus far for purposes of illustration. This relation can best be revealed with the aid of tabulated structural formulas.

TYPES OF MONO-SUBSTITUTION PRODUCTS

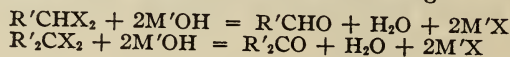
Hydrocarbon groups	Halides	Hydroxides	Amides
$-\text{CH}_3$	$-\text{CH}_2\text{X}$	$-\text{CH}_2\text{OH}$	$-\text{CH}_2\text{NH}_2$
$=\text{CH}_2$	$=\text{CHX}$	$=\text{CHOH}$	$=\text{CHNH}_2$
$\equiv\text{CH}$	$\equiv\text{CX}$	$\equiv\text{COH}$	$\equiv\text{CNH}_2$

Adopting a style of nomenclature that was originally, so far as the compounds here involved are concerned, applied to the hydroxides or alcohols, we distinguish the three types by designating them primary, secondary, and tertiary, respectively. For a long time this mode of distinction has also been applied to the corresponding halides, but not to the corresponding amides. It is right here that the irrationality of mixing systems of classification and nomenclature is keenly felt. For our purposes we shall, therefore, adhere rigidly to what appears to be the only rational solution of this confused condition. A primary mono-substitution product is a compound in which this substitution has taken place in connection with a methyl group of a hydrocarbon. A secondary compound, one in which the substitution has taken place in connection with a methylene group, and a tertiary compound, one in which it has taken place in connection with a methenyl group. Or in other words, using the structural groups tabulated above, a primary alcohol is a compound characterized by a $-\text{CH}_2\text{OH}$ group; a secondary halide, a compound characterized by a $=\text{CHX}$ group, a tertiary amide a compound characterized by a $\equiv\text{CNH}_2$ group.

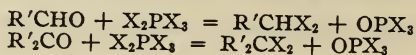
If it be continually borne in mind that these group formulas, like the complete formulas of chemical compounds, are but the chemical shorthand for the properties involved, no harm can result. It may not be amiss, therefore, to review a few of these properties, well known as they are. Using the most general expressions, they can be represented by the equations:



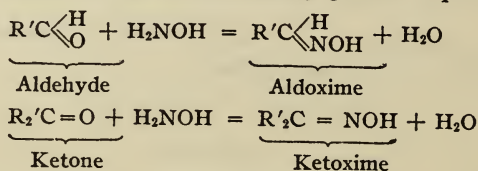
Here again genetic relationship becomes apparent as expressed by such well-known reactions as the following:



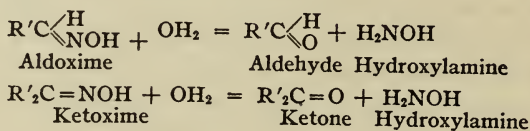
As is well known these reactions also are reversible:



If in place of the imides, resulting upon deammoniation from the diamides, we substitute their hydroxy or oxy derivatives, the oximes, the genetic relationship between aldehydes and ketones, on the one hand, and their respective oximes, on the other hand, is readily expressed by the following general equations:



Whereas the oximes result upon condensation, upon hydrolysis they may be caused to resolve into their components, hydroxylamine and either aldehyde or ketone.



TYPES OF TRI-SUBSTITUTION PRODUCTS

Hydrocarbon
groups



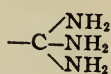
Halides



Hydroxides

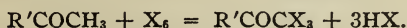


Amides

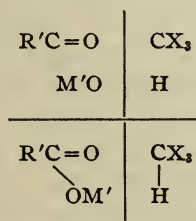


A number of well-known reactions might be cited to point out the genetic relationship indicated by the above group formulas. A few may suffice.

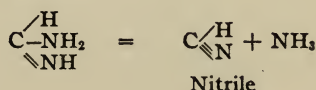
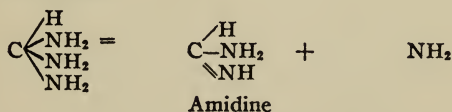
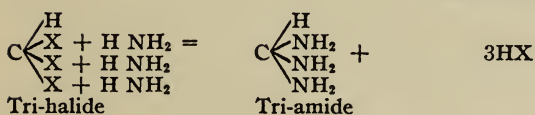
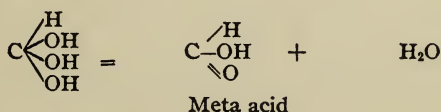
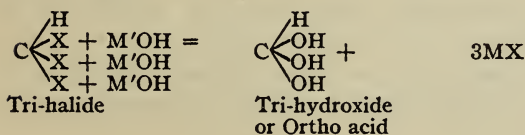
Under certain conditions all three hydrogen atoms of a methyl group can be replaced readily by halogen:



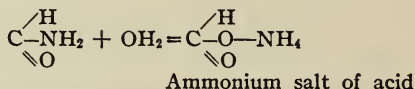
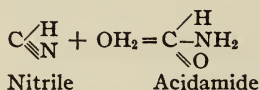
The above tri-halide is readily hydrolyzed to methenyl or formyl tri-halide (chloroform, bromoform and iodoform).



The trihalide thus resulting can be converted either into the tri-hydroxide or ortho acid and its dehydration product, the meta acid, or through the triamide into the corresponding amidine and nitrile.



The nitrile in turn can be hydrolyzed to the acid through the acid amide:

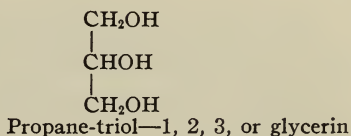
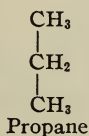


Other genetic relationships, as, *e. g.*, between mono-, di-, and tri-, substitution products, can be brought out. Thus the student in organic chemistry is taught that the difference between a primary, secondary and tertiary alcohol consists in this, that the primary alcohol can readily be oxidized to an aldehyde and an acid with the same number of carbon atoms, the secondary alcohol to a ketone, and that the tertiary alcohol is not capable of similar oxidation. This fact was first emphasized by Kolbe basing his structural notions on the type carbinol. Having abandoned the theory of types to a large extent, the above definitions have largely lost their structural significance, at least as brought out in textbooks. The structural significance is again emphasized, but from the unitarian point of view of our definition of organic chemistry, *viz.*, that organic chemistry is the chemistry of the hydrocarbons and their substitution products.

MULTIPLICATION OF TYPES

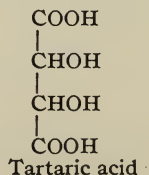
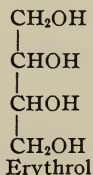
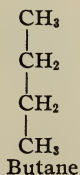
Thus far only those substitution products have been considered in which substitution has taken place in connection with the same carbon atom. It has already been pointed out that substitution in connection with different carbon atoms produces no new types but merely a multiplication of types already developed. This becomes apparent if we but recall that with the exception of methane all hydrocarbons are composed, so far as substitution is concerned, of the three simple groups used in developing types thus far studied. This *a priori* reasoning is in accord with the facts. A few relatively simple and well-known illustrations will clearly reveal this.

Thus, *e. g.*, glycerin is a tri-atomic alcohol in which the three hydroxy groups are associated one with each of the three carbon atoms as represented by the following formula referable to propane.

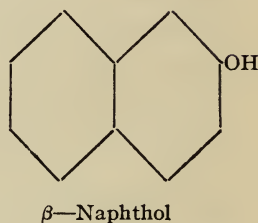
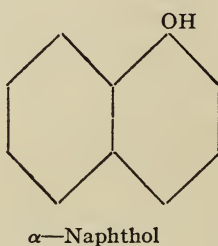
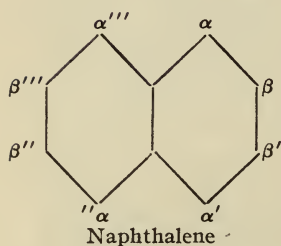
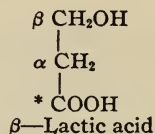
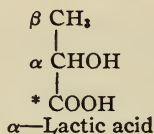


It is twice a primary alcohol and once a secondary alcohol and the above chemical shorthand expression is in accordance with the properties of this substance.

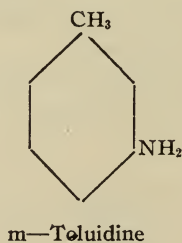
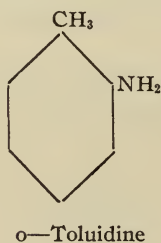
Erythrol is a similar tetratomic alcohol and some of its properties find expression in the formula of tartaric acid to which it can be oxidized.



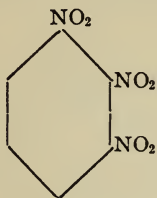
With the multiplication of types, it becomes necessary to indicate their position. This is done in a variety of ways. Thus the letters of the Greek alphabet have been used.



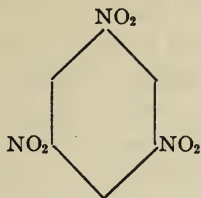
Abbreviations for neighboring (o = ortho), opposite (p = para), and intermediate (m = meta) were suggested by Kekulé to indicate the positions in connection with di-substitution products of benzene.



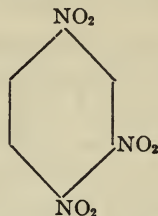
In connection with the tri-substitution products of benzene, the abbreviations for neighboring (v) = vicinal, (s) = symmetric and (a) = asymmetric were likewise suggested by Kekulé.



v—Trinitro benzene



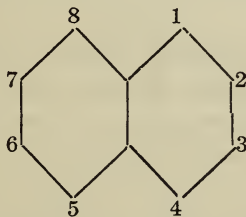
s—Trinitro benzene



a—Trinitro benzene

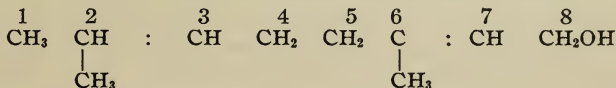
For more special purposes, special symbols have been suggested, as, *e. g.*, N for “Nor” derivatives of heterocyclic compounds, etc.

Numbers have also been used and are being used more and more. Thus the ten isomeric di-substitution products of naphthalene have long been indicated by numbers.



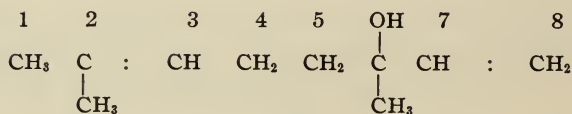
The Geneva Congress* suggested the exclusive use of numbers and no doubt, thereby prepared the way for a simpler nomenclature. Not only are numbers used to indicate the position of type groups, but of double bonds, the structural equivalents of hydrogen as well.

The application of these rules to recent structural research may best be illustrated with the aid of a few formulas.



Di-methyl-1,2,6-octa-diene-2,6-ol-8; or geraniol

* See Tiemann's account of the Congress in Ber. d. d. chem. Ges., 26, p. 1595. An abridged account can be found in Richter-Anschuetz-Smith, *Organic Chemistry*, 3rd Am. ed. (1899), vol. 1, p. 57.



Dimethyl-2,6-octadiene-2,7-ol-6; or linalool.

The nomenclature of organic chemistry naturally reflects basal theories and these again underlie classification. Hence rational nomenclature and classification go hand in hand. While the Geneva Congress paved the way, in part, for a more rational naming of carbon compounds, it could not get very far, because it had no rational classification as a necessary basis for its deliberations and rules. Hence it did not get beyond propositions for the nomenclature of chain compounds.

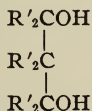
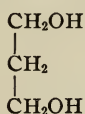
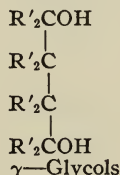
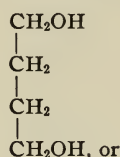
HETEROCYCLIC COMPOUNDS

Practically all carbocyclic compounds are readily taken care of when referred to the underlying carbocyclic hydrocarbons. How these can be classified has already been pointed out. Difficulty has arisen, however, in the classification of heterocyclic compounds. The conventional classification, or rather lack of classification, of these compounds is one of the serious drawbacks of our text and reference works on organic chemistry.

The most important of these are again those oxygen and nitrogen compounds containing one or more oxygen or nitrogen atoms in the cycle or ring. But it is a comparatively easy matter to classify them along rational lines, both of chemical structure and genetic relationship. As before, the oxygen compounds will be taken up first.

It has already been pointed out that hydroxy substitution in connection with different carbon atoms of the underlying hydrocarbons does not produce new types. This statement is true only in so far as the hydroxy substitution products themselves are concerned. This point has been illustrated by a few well-known formulas. It has also been pointed out that in such compounds the position of the substituting groups plays a more or less important role and should be considered in connection with the classification of these compounds.

Thus, *e. g.*, those glycols in which the two hydroxy groups are connected with different carbon atoms may be subclassified into alpha, beta, gamma, etc., glycols. Series of such glycols may be represented either by their initial members or by type formulas.

 α —Glycols β —Glycols γ —Glycols

Whereas those glycols which contain both hydroxy groups connected with the same carbon atom, as a rule, split off water very readily, thereby yielding aldehydes and ketones, respectively; those glycols in which the two hydroxy groups are connected with different carbon atoms split off the elements of water much more reluctantly. Moreover, the ease with which they split off water depends upon the position of the hydroxy groups. Thus, gamma, delta and epsilon glycols yield a molecule of water from the two hydroxy groups much more readily than do the alpha and beta glycols, for the reason that rings with five, six and seven members, are, as a rule, much more stable than those with three and four members.

The classification of these glycols and their corresponding oxides can best be demonstrated in two ways: first by their derivation from the underlying hydrocarbons, and secondly by the development of homologous series from the types thus established.

Hydrocarbons	α -Glycols	Oxides	β -Glycols	Oxides
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2 \backslash \\ \text{CH}_2 / \end{array} \text{O}$		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \backslash \\ \text{CH} / \end{array} \text{O}$ CH_3	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \backslash \\ \text{CH} / \end{array} \text{O}$ CH_2 CH_3	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_3 \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \backslash \\ \text{CH} / \end{array} \text{O}$ CH_2 CH_2 CH_3	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$

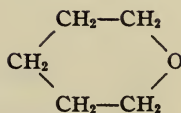
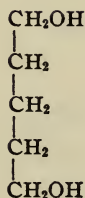
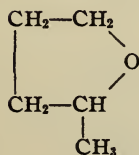
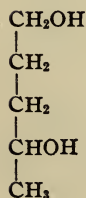
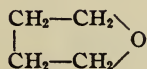
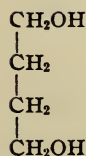
In the above table only those glycols and their corresponding oxides derivable from normal hydrocarbons have been recorded simply as a matter of convenience. Having established the types of glycols and oxides, it is an easy matter to take the first member of each series and use it as the starting point for the development of an homologous series.

γ -Glycols

Oxides

 δ -Glycols

Oxides



In a similar manner heterocyclic compounds with two oxygen atoms to the cycle can be referred to and derived from the glycols. Both the simple oxides (dimethylene oxide, trimethylene oxide, etc.) as well as the heterocyclic compounds with two oxygen atoms should be subordinated, for purposes of classification, to the glycols, as the monooxygen ethers are to the monatomic alcohols.

Hydrocarbons	α -Diamides	Cyclic Imides	β -Diamides	Cyclic Imides
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{NH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \quad \diagup \text{NH} \\ \text{CH}_2 \end{array}$		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CHNH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \quad \diagup \text{NH} \\ \text{CH} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2\text{NH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CHNH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \quad \diagup \text{NH} \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CHNH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_3 \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CHNH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \quad \diagup \text{NH} \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CHNH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$

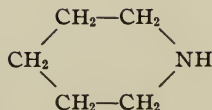
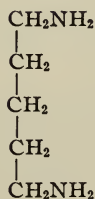
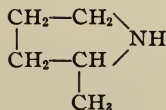
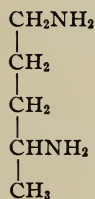
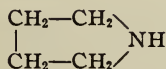
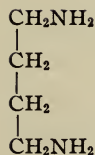
The same principle of classification applies to the heterocyclic compounds with one or more nitrogen atoms in the ring. Those with one nitrogen atom can be derived from the corresponding diamines by deammoniation as the oxides were derived from the

γ -Diamides

Cyclic Imides

 δ -Diamides

Cyclic Imides



glycols by dehydration. Like the alkyl derivatives of the monamines, these cyclic imines should be subordinated, for purposes of classification, to the corresponding diamines. The types of cyclic imines referable to diamines of the limit series are tabulated above.

APPENDIX A

ARRANGEMENT ACCORDING TO THE NUMBER OF
CARBON ATOMS

The arrangement of carbon compounds according to the number of carbon atoms or equivalents became possible only after a large number of organic compounds had been analyzed. In a way it may be regarded as the basal empirical classification, the importance of which might easily be overestimated when quantitateness was a dominant thought in chemistry. Strange as it may now seem, it does not appear that such an arrangement was seriously suggested immediately, even after Liebig had perfected the technique of organic analysis, thus making possible the determination of carbon atoms or carbon equivalents, much less shortly after the idea of quantitateness became the dominant idea in chemistry with the antiphlogistic theories of Lavoisier. It is rather significant that such an arrangement of organic compounds was carried out in all seriousness in one of the principal handbooks of chemistry only after the dogmatism of the first half of the nineteenth century had caused the partial shipwreck of organic theories.

The primary classification of carbon compounds according to the number of carbon atoms was put into practice in Lepold Gmelin's comprehensive and extensively used *Handbuch der Chemie*, the first edition of which had appeared in 1817, and which is best known to English speaking chemists through Watt's translation published by the Cavendish Society.

A conspicuous example of a modern text, or rather handbook, of chemistry in which the same primary classification occurs is the well known *Treatise on Chemistry* by Roscoe and Schorlemmer, volume three of which, the first part of organic chemistry, appeared in 1890.

APPENDIX B

CLASSIFICATION AS REVEALED BY TABLES OF CONTENTS

One of the earliest texts on chemistry devoid of alchemistic jargon is that of Lemery, the first edition of which appeared in 1675. It not only appeared in numerous editions during his life time, but its publication was continued long after the author's death. Moreover, it was translated into English, Dutch, German and Italian. For more than a century it exerted a decided influence on chemical thought. Like most books of historical interest, Lemery's *Cours de Chymie* is not generally available. For this reason, a small part of the table of contents (edition of 1756) is herewith reproduced:

LEMERY, *Cours de Chymie*

Des Minéraux

- I. De l'or.
- II. De l'argent, etc.

Des Végétaux

- I. Du jalap, résine ou magistère du jalap.
- II. De la rhubarbe, extrait de rhubarbe.
- V. De la canelle, huile ou essence de canelle, son eau étherée, tincture de canelle.
- XIX. Du sucre, esprit de sucre.
- XXI. Du vinaigre, distillation du vinaigre.
- XX. Du vin, distillation de vin et eau-de-vie, esprit de vin, etc.
- XXII. Du tartre, crystal de tartre, tartre soluble ou sel vegetal, crystal du tartre chalybé ou martial, tartre martial soluble, tartre emetique, etc.
- XXXII. Du camphre.

Des Animaux

- I. De la vipre, destillation de la vipre.
- V. Du miel, etc.
- VI. De la cire, etc.

The very limited scope of the organic *materia chemia* at the close of the 18th century becomes apparent from the following table of contents, viz. that of

F. A. C. Gren: *Grundriss der Naturlehre in seinem mathematischen und chemischen Theile neu bearbeitet.* 1793.

Bestandtheile der Koerper der drey Naturreiche (p. 255).

Mineralische Substanzen (p. 256): Die Koerper des Mineralreiches, oder die unorganischen Koerper lassen sich fueglich in fuef Classen abtheilen, nemlich Salze, Erden, Metalle, Erdharze, und Schwefel.

Bestandtheile der Pflanzenkoerper (p. 318): Zu den naeheren Bestandtheilen des Pflanzenreiches rechne ich:

- (1) Schleim oder Gummi
- (2) Harz
- (3) Kleber
- (4) Staerkeartigen Theil
- (5) Zucker
- (6) Weinsteinsaeure
- (7) Sauerkleesalzsaeure
- (9) Aepfelsaeure
- (10) Essigsaeure
- (11) Benzoesaure
- (12) Zusammenziehenden Stoff
- (13) Fettes Oel
- (14) Aetherisches Oel
- (15) Kampher
- (16) Scharfen Stoff und
- (17) Narcotischen Stoff.

Bestandtheile der thierischen Koerper (p. 344): Als naehere Bestandtheile des thierischen Koerpers sind bekannt:

- (1) Gallerte
- (2) Fett
- (3) Lymphe
- (4) Fadenartiger Theil
- (5) Knochenmaterie und
- (6) Milchzucker
- (7) Ameisensaure und
- (8) Das scharfe Harz der spanischen Fliegen.

Practically the same list of “naeheren Bestandtheilen, die als solche in Koerpern des Gewaechsreiches praeëxistirne” is enumerated in Gren’s *Systematisches Handbuch der gesamten Chemie* of 1794 (vol. 2, p. 3).

That the number of organic substances had grown but little shortly after Lavoisier’s death becomes apparent from the following list. Though Lavoisier’s point of view is primarily that of oxygen and combustion the distinction between vegetable and animal acids is clearly marked.

A. Lavoisier: *Traité élémentaire de chimie*, 1801.

Lavoisier’s point of view is that of oxygen: oxidation and combustion. Having considered the four simple combustible substances, *viz.*, phosphorus, sulphur, carbon, and hydrogen, he turns to the combustion of vegetable fats. This leads him to the consideration of “the composition of vegetable and animal substances” in general (I, p. 123). Those substances related to carbonic acid, the product of combustion, are naturally of prime interest to him. He names them, in accordance with his system of nomenclature of mineral acids, as follows:

Vegetable	Animal
L’acide acéteux	L’acide lactique
L’acide acétique	L’acide saccho-lactique
L’acide oxalique	L’acide bombique
L’acide tartareux	L’acide formique
L’acide pyro-tartareux	L’acide sébacique
L’acide citrique	L’acide prussique
L’acide malique	
L’acide pyro-muquex	
L’acide pyro-ligneux	
L’acide gallique	
L’acide benzoïque	
L’acide camphorique	
L’acide succinique	

The same point of view naturally leads him to take up next the products of destructive distillation (I, p. 132) of vegetable and animal substances, among which he mentions Dippel’s oil.

Inasmuch as carbonic acid is one of the principal products of the fermentation of saccharine liquids, the process of vinous

fermentation comes next (p. 139) to be followed by putrid fermentation (p. 153) and acetous fermentation (p. 159).

The consideration of acids is followed by that of the salts, the organic (pp. 277-322) following the inorganic (pp. 231-276).

A more compendious list is enumerated in the ten volume works of _____

A. F. Fourcroy: *Système des connaissances chimiques*, 1800.
On vegetable organic compounds (Volume 7).

1. Juice
2. Mucous, mucilage and gums
3. Sugar
4. Vegetable acids
 - A. "Acids natifs et purs."
 - (a) Gallic acid
 - (b) Benzoic acid
 - (c) Succinic acid
 - (d) Malic acid
 - (e) Citric acid
 - B. "Acidules"
 - (a) Oxalic acid
 - (b) Tartarous acid
 - C. "Acides empyreumatiques."
 - (a) Pyromucous acid
 - (b) Pyrotartarous acid
 - (c) Pyroligneous acid
 - D. Acids not found as such in nature
 - (a) Mucous acid
 - (b) Camphoric acid
 - (c) Suberic acid
 - E. Artificial acids corresponding to natural acids
 - (a) Malic acid
 - (b) Tartarous acid
 - (c) Oxalic acid
 - F. Acids produced by fermentation
 - (a) Acetous acid
 - (b) Acetic acid
5. Farinaceous substance
6. Gluten
7. Extractive
8. Fixed oil

9. Fat and wax
10. Volatile oil
11. Camphor
12. Resins
13. Gum-resins
14. Caoutchouc
15. Balsams
16. Pigments
17. Vegetable albumen
18. Woody substance
19. Tannin
20. Cork
21. Fossil and mineral substances

This classification according to the three natural kingdoms with the sub-classification of phytochemistry and zoochemistry not only extended to the systems of Berzelius and Liebig, but still finds its way into the lumber chambers of unclassified compounds of modern organic chemistries.* That it should have constituted the fundamental classification of phytochemistry as late as the seventies of the last century is, therefore, not surprising. The same conservatism went one step farther when pharmaceutical authors dignified this abandoned chemical point of view by calling it a "pharmaceutical" classification of chemicals.

To what extent organic chemistry was the chemistry of plant constituents even in 1837 becomes apparent from the following partial table of contents taken from Woehler's translation of Berzelius' *Lehrbuch der Chemie*.

NAEHERE BESTANDTHEILE PFLANZEN

- I. Klasse: Pflanzensauren (with thirty-three titles).
- II. Klasse: Vegetabilische Salzbasen (with twenty-two titles).
- III. Klasse: Indifferente Pflanzentoffe.
 1. Staerke
 2. Gummi und Pflanzenschleim
 - a. Gummi
 - b. Pflanzenschleim

* E. g., Richter-Anschuetz-Smith, vol. 2, pp. 334, et. seq.

3. Zucker

- a. Rohrzucker
- b. Traubenzucker
- c. Mannazucker
- d. Schwammzucker
- e. Suessholzzucker

4. Pflanzenleim und Pflanzeneiweiss

5. Pectin und Pectinsaeure

6. Pollenin

7. Fette Oele

- (c) Trockende Oele
- (2) Nicht " "
- (3) Feste Oele

Seifenbildungsprocess und seine Producte

- a. Eigentliche fette Saeuren, d. h. solche, welche bei der Destillation mit Wasser nicht mit uebergehen
- b. Durch den Seifenbildungsprocess erzeugte fluechtige Saeuren
- c. Glycerin oder Oelzucker
- d. Seife

Einfluss der Saeuren bei der Zersetzung der Oele

Fluechtige Oele

- a. Sauerstofffreie fluechtige Oele
- b. Sauerstoffhaltige " "
- (a) Aromatische Oele
- (b) Scharfe und blasenziehende Oele
- (c) Blausaeurehaltige giftige Oele
- (d) Campher

Harze

Extracte und extractfoermige Stoffe

- A. Rothe Pflanzenfarben
- B. Gelbe "
- C. Gruene "
- D. Blaue "

Skelett der Pflanzen

- a. Mark
- b. Holz und Pflanzenfaser
- c. Rinde

Von den fett-und harzhaltigen Milchsaeften der Pflanzen und den sogenannten Gummiharzen

Wurzeln

Rinden

Holzarten

Kraeuter und Schwaemme

Blaetter

Bluethen

Fruechte und Samen

APPENDIX C

DEFINITIONS OF ORGANIC CHEMISTRY

Gmelin. "The bodies of the organic kingdom are distinguished, in their most complete state, from those of the inorganic kingdom:

1. By their inherent vital force.
2. By a peculiar structure, internal and external.
3. By being composed, for the principal and most important part at least, of chemical compounds quite peculiar to them, called Organic compounds, or Proximate principles of the organic kingdom, which occur in the bodies of plants and animals, partly mixed and partly combined, both with one another and with certain inorganic compounds."

"The proximate principles into which an organic body may be resolved, either by mechanical or by chemical means, are partly inorganic, such as water, carbonic acid, and other mineral acids; partly organic. When the latter are of such a nature, that any attempt to decompose them further leads to the formation of decomposition products, which when reunited, produce something totally different from the substance originally decomposed, they are regarded as Primary, or Elementary Organic Compounds."

Handbook of Chemistry. Translation of the 4th edition. Vol. 7, p. 1.

Gerhardt. "Die organische Chemie hat die Aufgabe, die Koerper, welche durch die Verbindung dieser Elemente (namely carbon, hydrogen, nitrogen and oxygen, and occasionally sulphur, phosphorus, metals, etc.) entstehen, zu untersuchen, und zwar in Beziehung auf ihre Eigenschaften, ihre Zusammensetzung und auf die Gesetze, nach welchen ihre Verwandlungen erfolgen. Da alle organischen Verbindungen ohne Ausnahme Kohlenstoff enthalten, so koennte man die organische Chemie die Chemie

des Kohlenstoffs nennen. Sie betrachtet die organischen Substanzen nur in ihren rein chemischen Beziehungen, ohne Ruecksicht auf ihre Rolle im Organismus . . .”

“Alle Gebilde, Secretionen und Organe des Pflanzen- und Thierkoerpers sind Mischungen von organischen Stoffen in verschiedenen Verhaeltnissen. Die organische Chemie gibt die Mittel an, diese bestimmten Bestandtheile, deren Zusammensetzung unter denselben Umstaenden genau dieselbe und unveraenderlich ist, von einander zu trennen und sie in dem Zustande der Reinheit darzustellen. Sie allein gehoeren ins Gebiet der organischen Chemie.”

Grundriss de organischen Chemie. Aus dem Franzoesischen uebersetzt von A. Wurtz, Strassburg, 1844, vol. 1, pp. 142.

Kekulé. “Wir sind also zu der Ueberzeugung gelangt, dass die chemischen Verbindungen des Pflanzen- und Thierreichs dieselben Elemente enthalten wie die Koerper der leblosen Natur; wir haben die Ueberzeugung, dass in ihnen die Elemente denselben Gesetzen folgen; dass also weder in dem Stoff, noch in den Kraeften und ebensowenig in der Anzahl oder in der Art der Gruppierung der Atome ein Unterschied besteht zwischen den organischen und den unorganischen Verbindungen. Wir sehen eine fortlaufende Reihe chemischer Verbindungen, deren einzelne Glieder (wenn man nur die nahe liegenden vergleicht) eine so grosse Aehnlichkeit zeigen, dass naturgemaess nirgends eine Trennung gemacht werden kann. Wenn aber dennoch eine Trennung vorgenommen werden soll, wie sie in der That, einzig im Interesse der Uebersichtlichkeit, vorgenommen werden muss, dann ist diese Trennung an sich nicht natuerlich, sie ist rein willkuerlich und man kann eben darum die Grenze da ziehen, wo es gerade zweckmaessig scheint. Will man dabei so theilen, dass moeglichst das, was gewohnheitsmaessig in der organischen Chemie abgehandelt wurde, auch jetzt als besonderer Abschnitt abgehandelt werde, so erscheint es am zweckmaessigsten, wie dies in neuerer Zeit schon oefter vorgeschlagen wurde, alle Kohlenstoffverbindungen in diesem Abschnitte zusammen zu fassen.

“Wir definiren also die organische Chemie als die Chemie der

Kohlenstoffverbindungen. Wir sehen dabei keinen Gegensatz zwischen unorganischen und organischen Verbindungen. Das was wir mit dem althergebrachten Namen organische Chemie bezeichnen und was man zwechmaessiger Chemie der Kohlenstoffverbindungen nennen wuerde, ist vielmehr nur ein specieller Theil der reinen Chemie, den wir desshalb besonders abhandeln, weil die grosse Anzahl und die besondere Wichtigkeit der Kohlenstoffverbindungen ein specielleres Kennenlernen derselben noethig erscheinen laesst."

Lehrbuch der organischen Chemie, vol. 1, p. 10. A translation of this page may be found in Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. 3, Part 1, 32.

VOLUME I

(*Complete in five numbers, with title-page, table of contents, and index.*)

- No. 1. On the speed of the liberation of iodine in mixed solutions of potassium chlorate, potassium iodine, and hydrochloric acid, by Herman Schlundt. 1894. 33 p. 35 cents.
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